A STUDY OF THE INFRARED DICHROISM IN HIGHLY BRANCHED POLYETHYLENE

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Master of Arts

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by
Sonya Hau Wu
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by

Sonya Hau Wu

Approved by:

W. G. Funk
Chairman of Thesis Advisory Committee

Coates Williams
Dean of Graduate Study

James E. Johnson
Major Professor

Herbert J. Bowlby
Minor Professor

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TABLE OF CONTENTS

CHAPTER PAGE

LIST OF TABLES

LIST OF FIGURES

FIGURE PAGE

CHAPTER I

INTRODUCTION AND THE PROBLEM

INTRODUCTION

Many polymer systems, including polyethylene are used for molded articles of considerable industrial importance. Their mechanical and physical behavior are related to the physical structure of the polymer which, in turn, is manifested by the crystalline order of the polymer molecules.

THE PROBLEM

Statement of the Problem. This study was undertaken to prepare polyethylene films of a highly branched polymer which could be drawn various amounts. The various films were each investigated with respect to the density, the infrared dichroism, the degree of branching and the temperature of melting to provide information concerning the structural changes occurring as a result of heat and deformation treatments.

Importance of the Problem. Many of the heat and deformation operations employed in the fabrication of molded articles from polyethylene may modify the physical properties so as to give the articles more desirable characteristics. Such modifications may be explained in terms of the changes

in the structural elements of the polymer. Thus, the importance of such structural studies is obvious.

CHAPTER II

REVIEW OF THE LITERATURE

PREPARATION OF POLYETHYLENE

Several years before 1933, hydrocarbon polymers resembling polyethylene were prepared using high pressure. However, at that time, the product was not characterized as the ethylene polymer. The first synthesis of polyethylene was made by Facott and Gibson in 1933 (28). Since this synthesis, many studies have been made of the methods of preparation. Presently two main processes are used to polymerize polyethylene. These are called high pressure and low pressure polymerizations.

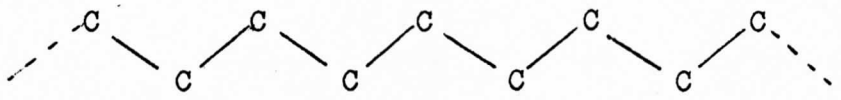
In the high pressure method, ethylene gas containing 0.01-5% oxygen is compressed to 500 atmospheres and maintained at a temperature of 200°C. After a certain reaction time, the pressure is released and solid polyethylene separates out (1). In this process, increased pressure increases the molecular weight of the product. Often diluents such as bezene, toluene, xylene, methanol and water can control the polymerization (5,6,8,25,30). Oxygen serves as a catalyst. Other catalyst systems, peroxide, peracid, and alkali metal persulfate, have been used (1).

In low pressure polymerization a catalyst such as tri-

methyl aluminum is employed at atmospheric pressure. The product has less short chain branching than the high pressure product.

PHYSICAL STRUCTURE OF POLYETHYLENE

The properties of polyethylene are determined largely by the structural features. The carbon skeleton of polyethylene is considered to be a planar zig-zag chain:



Branching in polyethylene was first suggested by Staudinger and Schulzin in 1935 (28,31) and confirmed by Alfrey, Bartovics and Mark (28,31). Intramolecular hydrogen transfer was suggested as the mechanism for short chain branching (28). Flory (9,10) proposed an intermolecular hydrogen transfer as the mechanism for long chain branching.

The effects of branching on the physical properties of polyethylene are very pronounced. Short chain branching effects crystallinity and therefore the melting range(28).

In general, polyethylene is a microcrystalline plastic with some disordered material. At room temperature, the elongation for the first 100% stretch is reversible. Tension larger than the critical value of about 600% stretch results in a permanent orientation (14).

Correlations between density and percent crystallinity have been made for polyethylene (17). Kojima and Abe (17) found that the specific volume, Vs and the fraction of crystalline material, x, are related by the empirical equation:

$$Vs = 1.233\ (1 - x) + 1.009\ x$$

An orientation study on drawn samples of polyethylene indicates that greater orientation at given elongation is achieved for quenched samples. The orientation is assumed to be produced by lamellar flow (15). At room temperature polyethylene which is drawn tends to have a chain alignment parallel to the draw direction (40).

In summary, the physical properties of polyethylene will depend on the average molecular weight, short and long chain branching, degree of crystallinity, and average orientation of the crystalline units.

INFRARED STUDY OF POLYETHYLENE

Infrared absorption has been found to be an important method for structural study. It has been extensively used (1,3,7,16,18,20,22,23,27,29,32,33,34,36,37). Absorption bands from 70 to 3000 $cm.^{-1}$ have been studied and assigned (1,20,33). The absorption between 721 and 731 $cm.^{-1}$ and 1300 to 1500 $cm.^{-1}$ are of particular importance.

The bands at 721 and 730 $cm.^{-1}$ are characteristic of solid polyethylene and thus can be used to study the phase

changes as a function of temperature. They are useful in studying the melting point range for polyethylene. When the sample melts the doublet band (721 and 731 $cm.^{-1}$) is replaced by a broad band at 721 $cm.^{-1}$ (1,20,33).

The absorption band at 1310 $cm.^{-1}$ is assigned as an amorphous band (16). The 1375 $cm.^{-1}$ band is due to a CH_3 absorption.

By use of the extinction coefficient of the 1375 $cm.^{-1}$ band, Bryant (3,4) has calculated the degree of branching in samples of polyethylene films. Stephan and Varga (32) use the relative absorptions of the 1375 and 1470 $cm.^{-1}$ bands to determine the degree of branching.

The use of polarized infrared radiation for structure analysis was first suggested by Elliott et al(7). The dichroic ratio is defined by Gailey (11) as the ratio of the absorbancies of an absorption band when the electric vector of the plane polarized beam at normal incidence is first parallel and then perpendicular to the stretching direction. A number of studies on the infrared dichroism of polyethylene have been made (37,18,24). The vibrational spectrum of polyethylene is shown in Tables I and II.

TABLE I

INFRARED ABSORPTION BANDS OF POLYETHYLENE (1)

wave-length	wave number	Assignment	Dichroic Properties
microns	$cm.^{-1}$		
3.38	2958	Unsymmetrical stretching in methyl groups	No dichroism
3.42	2920	Unsymmetrical stretching in methylene groups	Weak perpendicular dichroism
3.48	2880	Symmetrical stretching methy groups	Weak perpendicular dichroism
3.51	2858	Symmetrical stretching in methylene groups	Weak perpendicular dichroism
3.36	2735	Methyl groups	
3.74	2678	Methylene groups	
6.79	1470	Deformation of methylene groups perpendicular to chain axis.	Perpendicular dichroism in all three bands
6.82	1465		
6.84	1463		
6.87	1458	Deformation of methyl group	No dichroism
7.25	1375	Symeetrical deformation of methyl group	No dichroism
7.30	1372		
7.39	1355	Deformation of methylene	Parallel dichroism
7.45	1340		
7.68	1300		
11.22	890	Rocking of methyl groups	
13.70	730	Rocking of methylene groups perpendicular to chain direction	Perpendicular dichroism

TABLE II

INFRARED SPECTRUM OF SOLID MARLEX 50 POLYETHYLENE (23)

wave number	Description	Phase	Interpretation (wave number in $cm.^{-1}$)
720	vs ⊥ b	A,C	b_{2u} fundamental
731	vs ⊥ a	C	b_{3u} fundamental
890	vvw		$R\overline{=}CH_2$
990	w ⊥	A,C	$RCH{:}CH_2$
1050	vw, sh //	C	
1077	vw, b	A	fundamental, amorphous p.e.
1176	vw, sh //	C	
1306	v,b //	A	fundamental amorphous p.e.
1352	m //	A	fundamental, amorphous p.e.
1367	m //	A,C.	b_{1u} fundamental
1463	vs ⊥ b	A,c,	b_{2u} fundamental
1473	vs ⊥ a	C	b_{3u} fundamental
1640	vw	A,C	C:C
1818	vw	A,C	1816 = 2 x 908
1894	w ⊥	C	726 + 1168 = 1894
2016	w //	A,C	726 + 1295 = 2021 (//)
2144	vw	A,C	726 + 1415 = 2141 (//)
2221	vw		1061 + 1131 = 2192
2242	vw	C	2 x 1131 = 2262
2275	vw	C	1131 + 1168 = 2299
2328	w		2 x 1168 = 2336 890 + 1168 = 2336
2345	w	A,C	1061 + (1306) = 2367 908 + 1440 = 2348 (1061 + 1295 = 2356)
2415	vw	A,C	1061 = 1367 = 2428 (//) 1061 + (1352) = 2413
2635	m	C	1168 + 1468 = 2636
2658	m		1295 + 1367 = 2662
2897	w		1440 + 1468 = 2908
4106	m ⊥		1295 + 2851 = 4146 (∥) 1168 + 2919 = 4087 (⊥)
4327	m ⊥		1415 + 2919 = 4334 (//) 1468 + 2883 = 4351 (⊥) 1440 + 2919 = 4359 (⊥)

CHAPTER III

EXPERIMENTAL INVESTIGATIONS OF THE ORIENTATION IN POLYETHYLENE

MATERIALS AND EQUIPMENT

For the studies, low density, highly branched polyethylene having a molecular weight of approximately 70,000 was supplied by the Chemistrand Research Center. Technical grade xylene as the polymer solvent, and mixture of carbon tetrachloride and benzene for the density determinations were used. In addition, a thermoregulated constant temperature water bath controlled at 25.5 $\pm$ 0.1°C; 3" x 3" glass plates, Appolo Ferrotype plates; and a Vari-Heat hot plate were used. A stretching frame especially designed for the orienting of polymer films previously described (21) was used to stretch the polyethylene films. The infrared spectra of the oriented films were obtained by means of a Beckmann Infrared Spectrophotometer, IR-7, used in association with a Beckmann silver chloride polarizing element, a specially disigned microsample holder also previously described(21) and a beam condenser with sodium chloride condensing lenses.

Finally, for obtaining the infrared spectra of polyethylene films as a function of temperature, a Perkin-Elmer Heating cell with polished sodium chloride disks and thermo-

couple assembly was employed in association with the Beckmann Infrared Spectrophotometer, IR-7.

SAMPLE PREPARATION

Two methods were developed to prepare the polyethylene films required for this study. In the first method, approximately 1.5 g. of polyethylene in the form of pellets were placed on 3" x 3.5" Appolo Ferrotype plate. The plate with the pellets was then placed on the hot plate, and the temperature of the hot plate increased until the polymer melted. The hot plate was turned off, and the melted polymer was covered by another Ferrotype plate. Pressure was then applied to the top plate to spread the molten polymer uniformly. The Ferrotype plate with molten polymer was then dropped quickly into water at room temperature. Upon removing the plates, coherent films having thicknesses between 0.4mm and 0.7mm. were obtained.

In the second method, a 3% by weight polyethylene-xylene mixture was obtained by dissolving the polymer in xylene at about 100°C. Approximately 2 ml. of this solution was poured on a 3" x 3" galss plate. The plate and solution was then placed in an oven maintained at 110°C. After the solvent evaporated, films approximately 0.01 mm. thick were obtained.

PREPARATION OF ORIENTED FILMS

1.5 cm. width strips were cut from the melt cast films. The ends of these strips were then clamped into the jaws of the stretching frame, then drawn to various lengths.

The drawn samples were removed from the stretching frame and allowed to relax for 24 hours after which the draw ratio was determined. Draw ratios were calculated from the formula:

$$\text{Draw Ratio} = (l - l_o) / l_o$$

where l, and l_o are the lengths after and before stretching, respectively.

DETERMINATION OF THE DENSITIES OF THE POLYETHYLENE FILMS

The densities of the films used in this study were measured by a flotation method. In this method, a small piece of the film was placed in a test tube containing carbon tetrachloride. The test tube was then placed in water bath at 25.5°C. so as to bring the system to thermal equilibrium. Benzene was then added to the test tube with stirring until the film was located about 1/6 of the way from the top of the liquid surface. The density of the solution was considered to be equal to the density of the film. The

density of the benzene-carbon tetrachloride solution was then determined at 25.5°C. by means of a pycnometer. This density was recorded as the film density.

As will be shown later, these density values were used to determine the percent crystallinity. These calculations are based on the principle that the specific volumes of the crystalline and the so called "amorphous" regions of the polymer are additive.

The derivation of the relation between percent crystallinity and density is given in the following:

Let Vx, Vc and Va be the specific volumes of polymer, completely crystalline, and completely amorphous substances, respectively. If ϕ is the fraction of crystalline material in the polymer, then

$$Vx = \phi\, Vc + (1-\phi)\, Va$$

Since $V = 1/\rho$, we have

$$\frac{1}{\rho_x} = \phi \frac{1}{\rho_c} + (1-\phi) \frac{1}{\rho_a}$$

$$\phi = \frac{\rho_c (\rho_x - \rho_a)}{\rho_x (\rho_c - \rho_a)}$$

From x-ray diffraction studies (12) the accepted values for polyethylene are $\rho_c = 1.014$ g/ c.c. and $\rho_a = 0.855$ g/c.c.

Substitution of these values give:

$$\phi = \frac{1.014\ (\rho_x - 0.855)}{\rho_x\ (0.159)}$$

$$= \frac{1.014}{0.159}\ \left(1 - \frac{0.855}{\rho_x}\right)$$

$$\% \text{ crystallinity (K)} = 100\,\phi = \frac{101.4}{0.159}\,.\left(1 - \frac{0.855}{\rho_x}\right)$$

$$\% K = 633.7 - \frac{545.2}{\rho_x}$$

By means of this equation, the % crystallinities for the oriented polyethylene films were calculated.

INFRARED STUDIES OF POLYETHYLENE FILMS

Characteristic Spectrum of Polyethylene Films. An unoriented polyethylene film 0.01 mm. thick obtained by casting from xylene solution was placed in the sample holder so as to receive the unpolarized infrared beam. Conditions of gain and scanning speed found to give optimum resolution of the absorption effects in double beam operation were used. By this means the infrared absorption spectrum of the polyethylene film was recorded between 600 $cm.^{-1}$ and 4000 $cm.^{-1}$ The various absorption bands were indexed with respect to wave number and recorded.

Determination of Degree of Branching. The degree of branching may be expressed in terms of number of CH_3/ 100 carbon atoms by the equation:

$$CH_3 \text{ / } 100\ C = 0.150\ K'$$

Where K is the specific absorption coefficient per cm. length for a concentration of one gram per cubic centimeter of polymer at 1375 $cm.^{-1}$

$$K' = \frac{1}{\rho L} \log \frac{I_o}{I}$$

Where ρ is the density of the polymer in grams/cc, L is the thickness of the polymer film in cm., and $\log (I_o/I)$ is the absorbance after background correction has been made. From measurements of absorbance, film density and film thickness, the degree of branching for this polyethylene sample was calculated.

Polarized Infrared Investigations of Oriented Films. Drawn films were placed, in turn, in the microsample holder, positioned between the beam condenser lenses which was placed behind the silver chloride polarizer. Spectra were obtained from 600 to 4000 $cm.^{-1}$ with the draw direction first parallel and then perpendicular to the plane of the polarized infrared beam. For the dichroic ratio measurements the absorption band at 2030 $cm.^{-1}$ was used. The dichroic ratio, R, is defined as the ratio of the absorbance in the parallel direction, $A_{//}$, to the absorbance in the perpendicular position, $A_{\perp}$

$$R = \frac{A_{//}}{A_{\perp}} \qquad (11,38)$$

Dichroic ratios were determined for all of the drawn

samples. These were recorded together with percent crystallinity and draw ratio data.

In addition, the average angles of orientation for these samples were calculated from:

$$\Theta = \tan^{-1}\sqrt{2R} \qquad (21)$$

Where Θ is the average angle of orientation and R is the dichroic ratio. These values were recorded, also. Plots of dichroic ratio and Θ versus draw ratio and percent crystallinity were made.

Estimation of the Infrared Melting Range for Polyethylene. For these studies a heating sample assembly obtained from Perkin-Elmer Corporation was used in association with unpolarized infrared radiation from a Beckmann Infrared Spectrophotometer, IR-7. The heating assembly consists of a cell of polished sodium chloride disks inserted in a heating element with a pre-calibrated thermocouple.

The film was sandwiched between the sodium chloride disks and placed in the heating element. This assembly was then inserted so as to receive the infrared beam. Spectra at various temperatures ranging from 30 to 160°C. were obtained. The transmittance of the absorption of the 720 $cm.^{-1}$ absorption band was plotted versus temperature.

CHAPTER IV

RESULTS AND DISCUSSION

Preparation of Films. The films cast from the melt were fairly uniform and had thicknesses ranging from 0.4 to 0.7 mm. These films were used for obtaining the oriented parameters. Solution cast films were too thin for drawing purposes.

In the initial drawing experiments, it was observed that some of the initial elongation imparted to the films was lost. It is believed that the highly branched samples have greater entropy effects which lead to a greater relaxation of the chain molecules from their constrained position. This is similar to what occurs when a stretched rubber band is released. Because of this, draw ratios were not computed until the relaxation process was completed. The original length, l_o, the final length, l, and the draw ratio for the eight films drawn are listed in Table III. In Table IV. the draw ratios, densities, and calculated percent crystallinities are given. The density values show that there are slight increases of density, 0.9076 g/c.c. to 0.9158 g/c.c., and % crystallinities, 37 to 42%, for increasing draw ratios ranging from 0.1 to 3.5. It is worth noting in this respect that the percent crystallinity (37 - 42%) is much lower than the crystallinity of the

TABLE III

THE ORIGINAL LENGTH, FINAL LENGTH AND DRAW RATIO FOR VARIOUS SAMPLES

Sample number	Original length, l_o	Final length, l	Draw Ratio
1	1.0 cm.	1.1 cm.	0.1
2	1.0 cm.	1.5 cm.	0.5
3	1.0 cm.	2.8 cm.	1.8
4	1.0 cm.	3.3 cm.	2.3
5	1.0 cm.	3.8 cm.	2.8
6	1.0 cm.	3.9 cm.	2.9
7	1.0 cm.	4.2 cm.	3.2
8	1.0 cm.	4.5 cm.	3.5

TABLE IV

THE DRAW RATIO, DENSITY AND PERCENT CRYSTALLINITY OF DRAWN POLYETHYLENE FILMS

Sample	draw ratio	density	% crystallinity
1	o.1	0.9076 g/cc	37
2	0.5	0.9088	38
3	1.8	0.9144	41
4	2.3	0.9150	42
5	2.8	0.9164	43
6	2.9	0.9156	42
7	3.2	0.9155	42
8	3.5	0.9158	42

Zeigler type polyethylene. Marlex 50, for example, have crystallinities of about 95%. It is assumed that this lower degree of crystallinity for this sample is due to the branching of the polyethylene. In view of this lower crystallinity it is suggested that a great deal of short chain branching exists in this polymer sample. It is also interesting to note that an alignment of the chain molecules has caused a slight increase in the amount of ordering in this particular polyethylene. It is to be noted also that after a draw ratio of 2.3 there is no significant increase in the crystallinity.

Infrared Spectrum and Determination of the Degree of Branching. Figure 1 is an infrared absorption spectrum of the highly branched polyethylene obtained with a Beckmann IR-7 Infrared Sepctrophotometer from 600 to 4000 $cm.^{-1}$ The film used was one casted from xylene sloution. Only five absorption bands are apparent, 720, 730, 1375, 1470, and 2940 $cm.^{-1}$ By the use of 1375 and 1470 $cm.^{-1}$ bands, the degree of branching was obtained. This was done by using the equation derived by Stefan:

$$CH_3/100\ C = \frac{1}{S + 1} \times 100 \quad (32)$$

where $S = A_{1470\ cm.^{-1}} / A_{1375\ cm.^{-1}}$

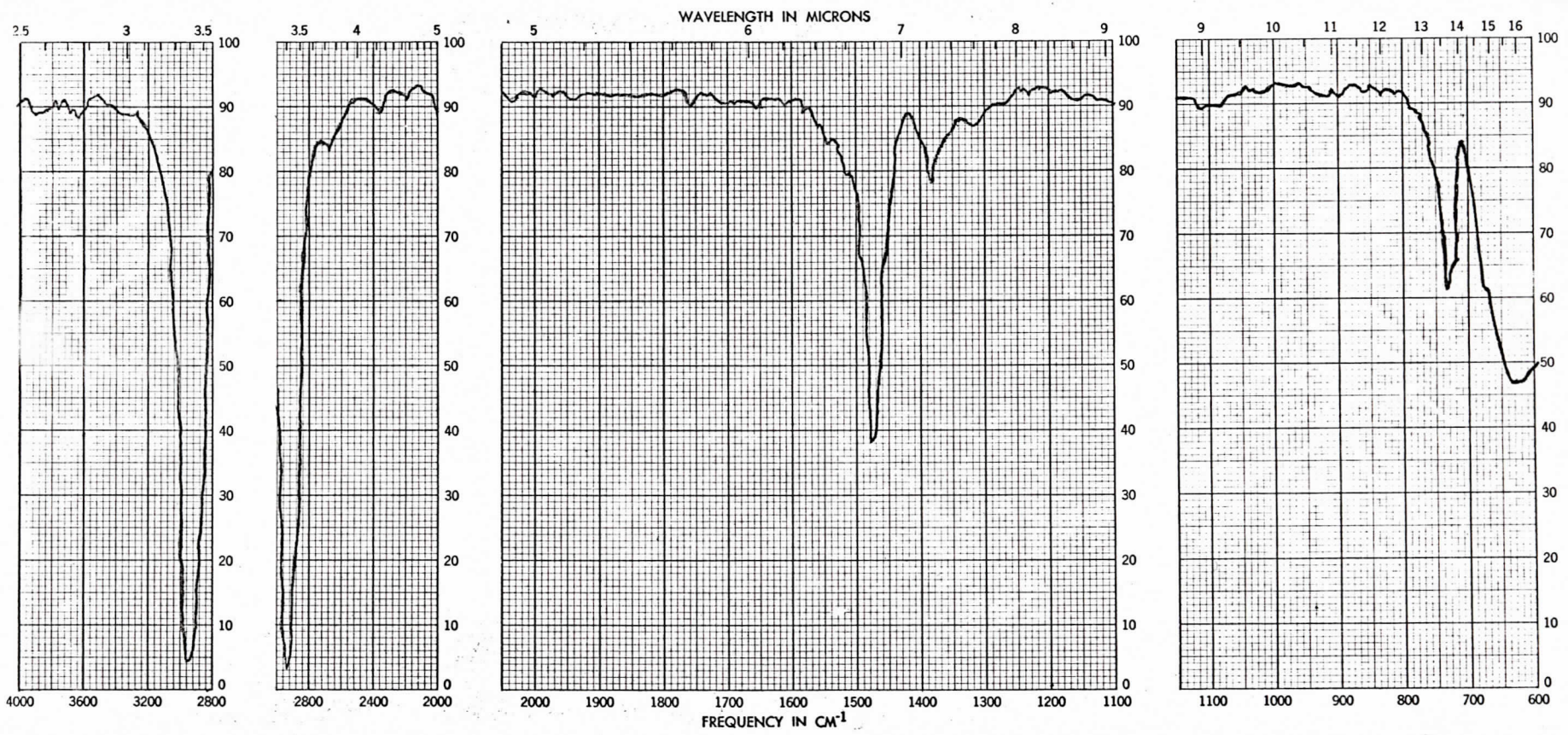


Figure 1

Infrared Absorption Spectrum of
Highly Branched Polyethylene

In this measurement, the integrated intensities of the 1470 and 1375 $cm.^{-1}$ bands were obtained by determing the areas under each of these curves. These data are given in Table V, for six different samples. The average value is found to be 12.7 CH_3 groups per 100 carbon atoms.

Figure 2 and 3 are the parallel and perpendicular polarized infrared absorption spectra for a polyethylene film having a draw ratio of 2.9 x.

In Table VII the dichroic ratio, average orientation angle, θ , for the 2030 $cm.^{-1}$ absorption band, together with draw ratio, density, and % crystallinity for the drawn samples are summarized.

Using the equation derived by Bryant (4), the degree of branching was calculated. Data are given in Table VI for two samples. The average value is 12.83 CH_3/100 carbon atoms. The deviation between the two methods is less than 1%.

TABLE V

RELATIVE ABSORPTION AT 1375, 1470 $cm.^{-1}$ BANDS

sample	area under 1470 $cm.^{-1}$	area under 1375 $cm.^{-1}$	ratio
1	8.7	63.6	7.42
2	9.4	65.0	6.91
3	8.95	63.45	7.09
4	14.1	91.8	6.51
5	13.8	92.2	6.68
6	13.7	94.7	6.91

Average ratio = 6.86

CH_3/100 C = 12.72

TABLE VI

CALCULATION OF DEGREE OF BRANCHING
BY BRYANT'S METHOD

sample	I	II
Thickness	0.00104 cm.	0.00115 cm.
Density	0.906 g/cc	0.906 g/cc
I_o	62.5	63
I	51.8	51.2
CH_3/100C	12.72	12.93

Average CH_3/100 C = 12.83

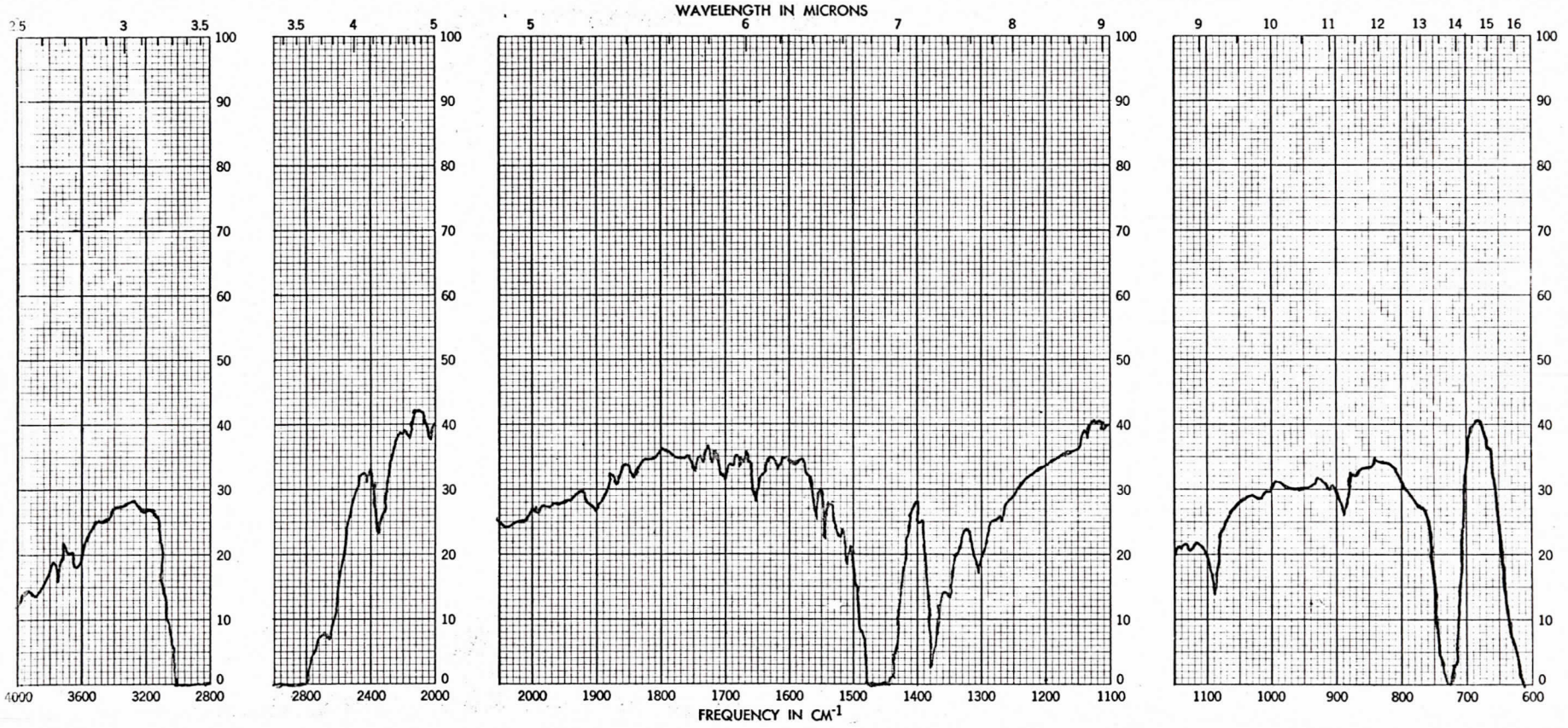


Figure 2

Parallel Polarized Infrared Absorption Spectra
for a Polyethylene Film Having a Draw Ratio of 2.9

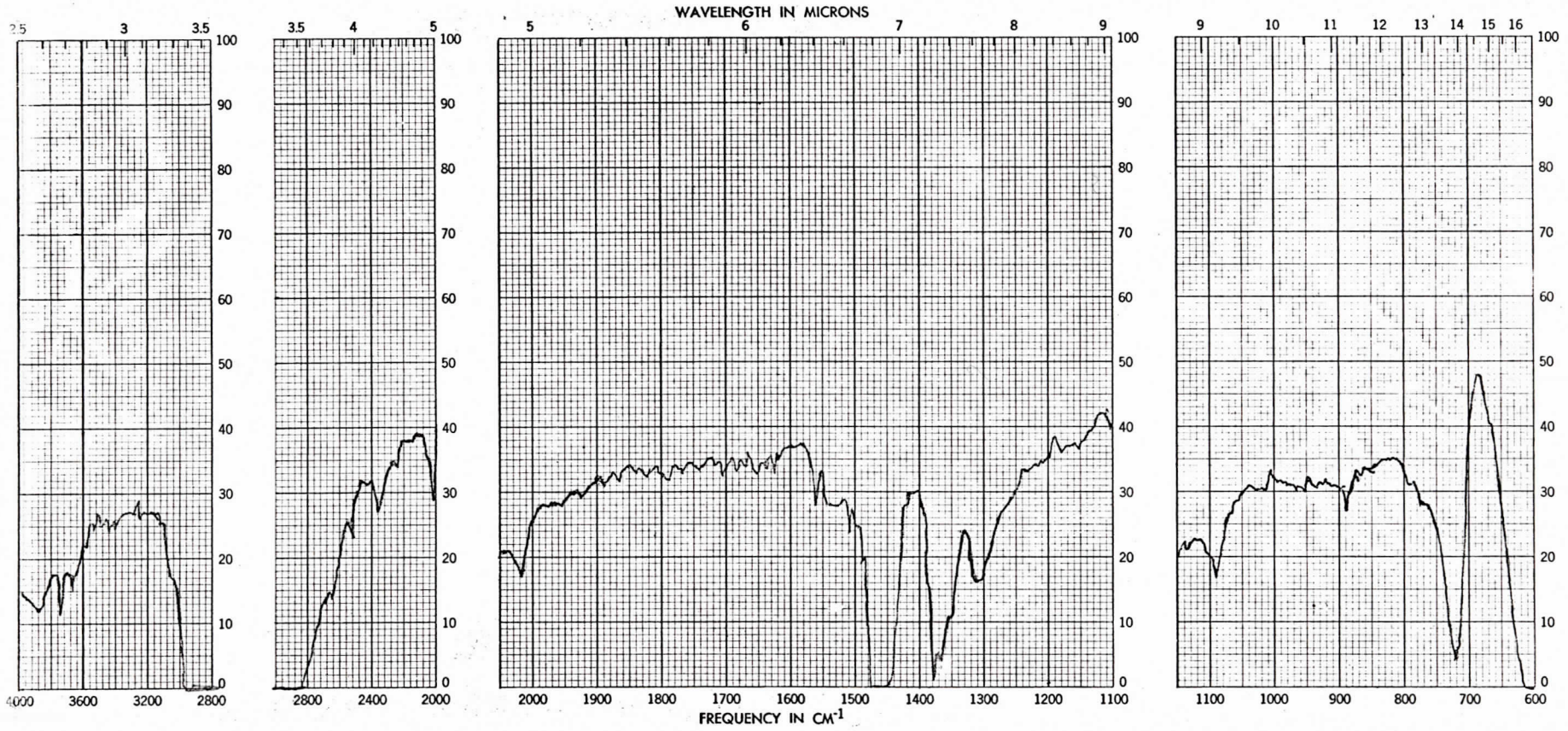


Figure 3

Perpendicular polarized Infrared Absorption Spectra
for a Polyethylene Film Having a Draw Ratio of 2.9x

TABLE VII

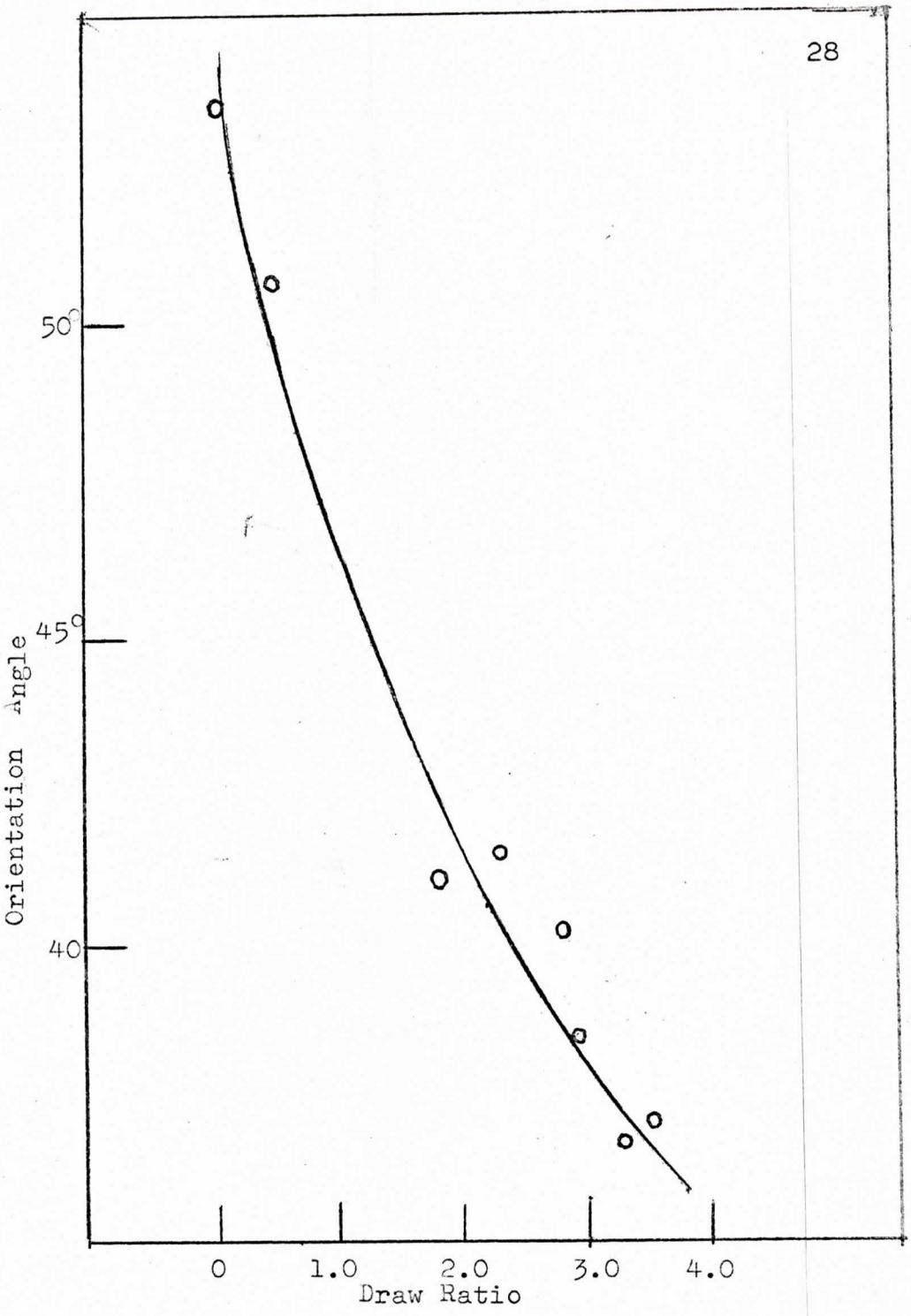
STRUCTURAL PARAMETERS OF DRAWN POLYETHYLENE FILMS
(Average CH_3/100 C = 12.7)

Sample	draw ratio	density	% crystallinity	dichroic ratio	θ
1	0.1	0.9076	37	1.1	53.5
2	0.5	0.9088	38	1.3	50.7
3	1.8	0.9144	41	2.6	41.1
4	2.3	0.9150	42	2.6	41.5
5	2.8	0.9164	43	2.8	40.2
6	2.9	0.9156	42	3.2	38.5
7	3.2	0.9155	42	3.6	36.8
8	3.5	0.9158	42	3.5	37.1

Figure 4 is a plot of average orientation angle versus draw ratio. Figure 5 is a plot of orientation angle versus degree of crystallinity. The two plots show an inverse relationship between Θ and draw ratio and between Θ and degree crystallinity.

Finally, the results of the change in the transmittance of the 720 $cm.^{-1}$ absorption band for different tempertures is shown by Figure 6. Here the temperature of the polyethylene is plotted versus % transmittance. The curve shows that from 30°C. to about 90°C. the transmittance increases from about 15% to 25%. From 90°C. to about 120°C., no change in transmittance occurs. This corresponds to the melting range for this polyethylene sample. From about 120°C to 160°C. there is a further increase in the transmittance.

In the first part of the curve from 30° to 90°C., the heat capacity of the polymer is increasing with increasing temperature. This is being brought about because more and more vibrational degrees of freedom are brought into play. This in turn is producing an increase in the disordering of the polymer structure. From 90° to 120°C., heat is being absorbed to melt out the crystalline regions. The wide range of melting is indicative that there is a rather wide range of sizes of the crystallite units or at least a wide range of different strengths of intermolecular attractions



Relation Between Draw Ratio and Orientation Angle

Figure 4

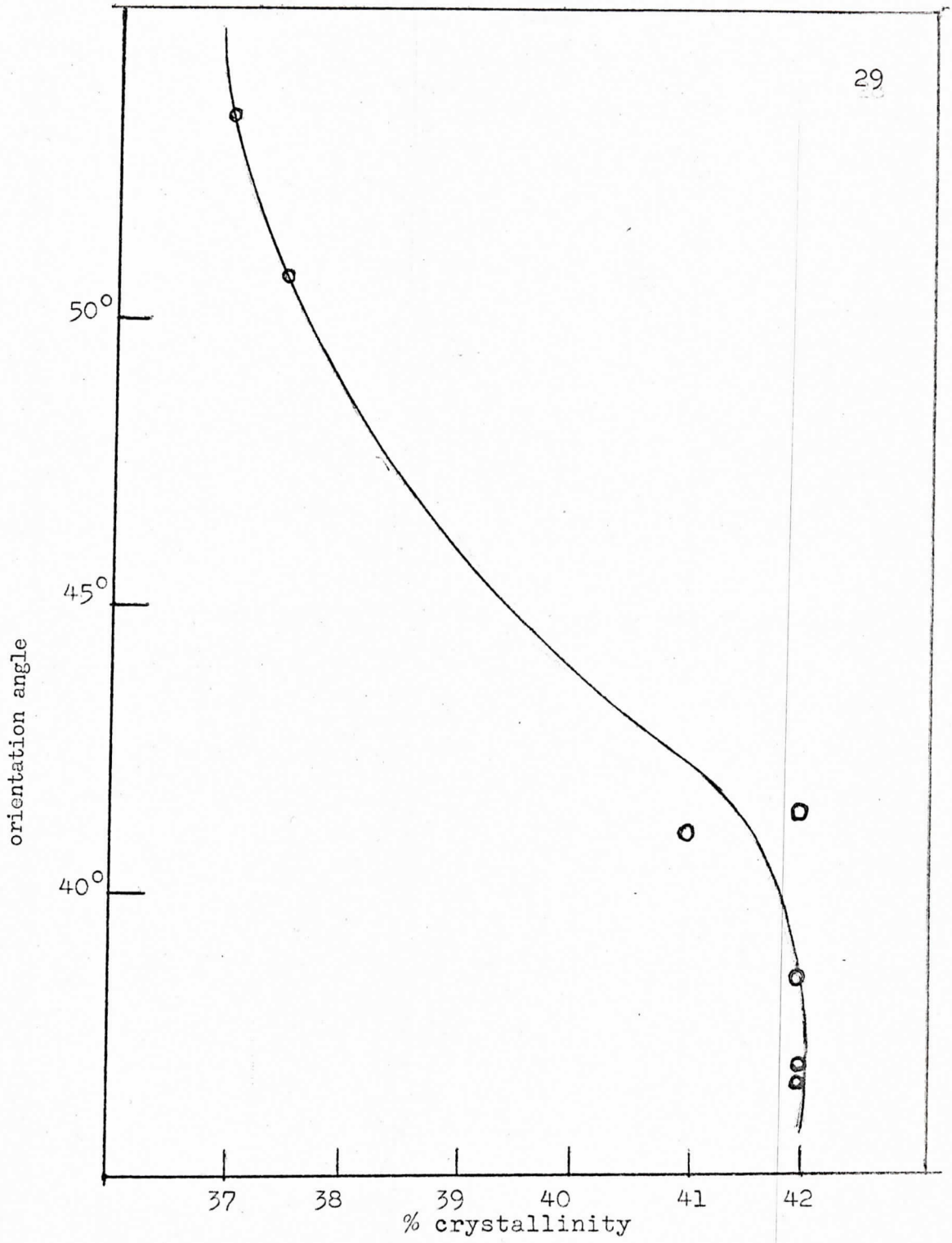


Figure 5

Relation Between % Crystallinity and Orientation Angle

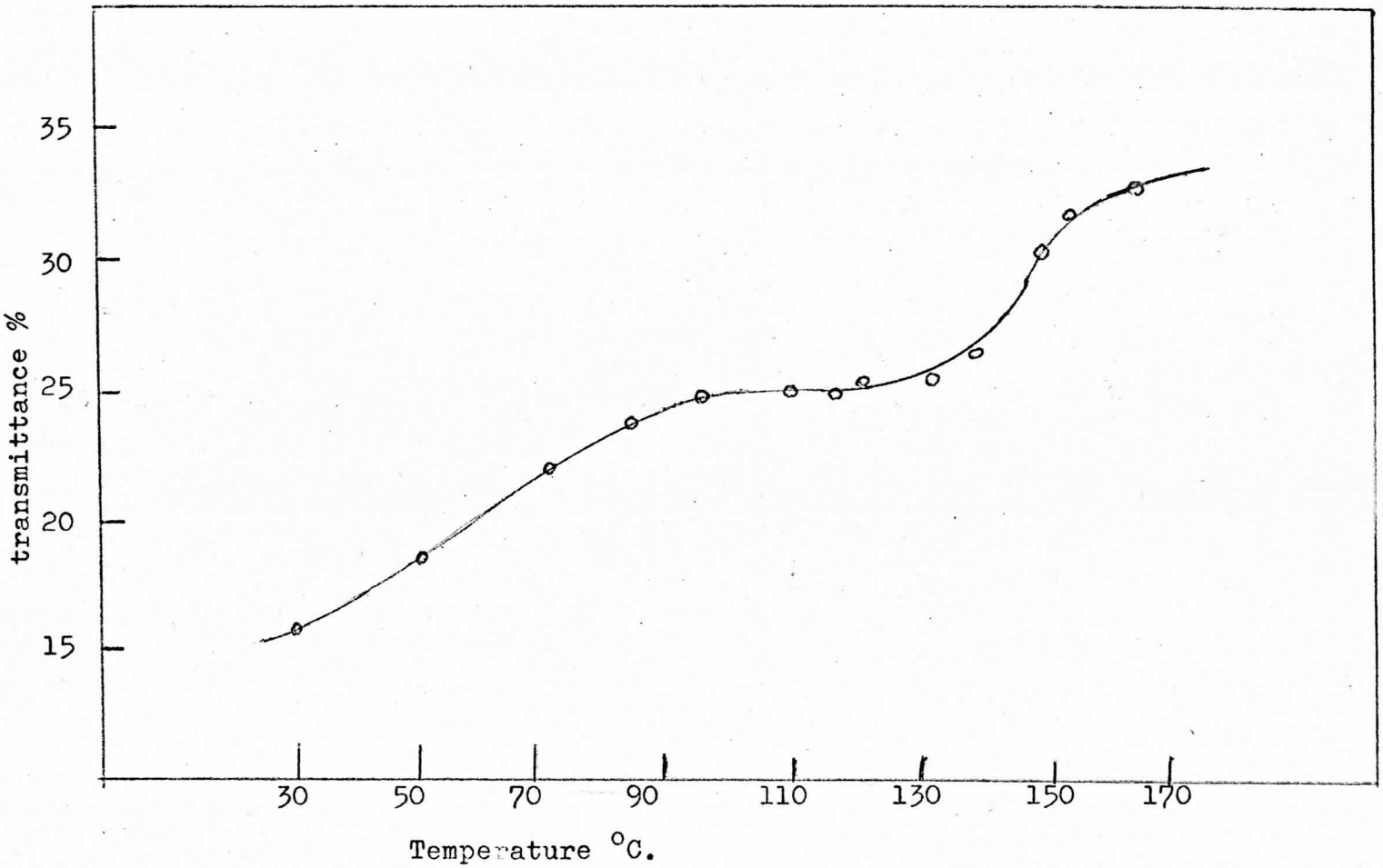


Figure 6

The Relation Between Temperature and Transmittance of 720 cm.$^{-1}$ Absorption Band for Polyethylene

attractions between chain molecules. From 120 to 160°C., there is once again an increase in heat capacity with increasing temperature. The sigmoid shaped curve in this region is suggestive that even in the melt there is some preferential arrangement of the polyethylene chains which, of course, continues to decrease with increasing temperature.

From this study the melting range of polyethylene lies between 90°C. and 120°C. The literature gives for the melting point of high pressure polyethylene a value of about 105°C. In contrast, Marlex 50 polyethylene melts at about 130°C. Thus, the effect of branching on the melting point of polyethylene can be seen to be consistent with crystallinity estimates made in this study.

CHAPTER V

SUMMARY AND CONCLUSIONS

SUMMARY

Investigations have been made on a sample of branched polyethylene (molecular weight 70,000) to conrrelate % crystallinity and draw ratio with average angle of orientation, θ , as determined by a measurement of the infrared dichroism of the 2030 $cm.^{-1}$ absorption band. In addition, the degree of branching has been determined by an infrared absorption method. Finally, by an infrared analysis of the 720 $cm.^{-1}$ absorption band as a function of temperature, the melting range for this highly branched polyethylene sample was determined.

In these studies, polyethylene films were prepared by melt and solution casting. Films were subsequently stretched to various draw ratios. Densities were measure by a flotation method, and dichroic ratios were determined by an infrared analysis of the 2030 $cm.^{-1}$ infrared absorption band using polarized infrared radiation from a Beckmann Infrared Spectrophotomer, IR-7. Degree of branching was determined with the 1375 $cm.^{-1}$ absorption band according to the method of Bryant(4). Finally transmittance of the 720 $cm.^{-1}$ absorption band at different temperatures ranging from

30 to 160°C were measured.

It was found from this study that densities ranged from 0.9076 g/cc to 0.9158 g/cc. These gave % crystallinity values 37-42% for draw ratios from 0.1 to 3.5. Dichroic ratios ranged from 1.1 to 3.5 and these gave orientation angles from 53.5° to 37.1°. The average degree of branching was found to be 12.7 CH_3/100 C. Finally the melting range was found to be between 90 and 120°C.

A plot of orientation angle versus draw ratio and percent crystallinity showed positive correlations. In both of these plots, orientation of the crystallinities increases (orientation angles decreases) with increased draw and increased percent crystallinity.

These structural parameters are discussed in terms of the degree of branching for this polyethylene sample.

CONCLUSIONS

As a result of this investigation, the following conclusions may be drawn:

1. The polyethylene sample possesses a reasonably high degree of branching (12.7 CH_3/100 Carbon atoms).

2. Density, degree of crystallinity, and crystallite orientation increase with increased drawing of the polyethylene film.

3. The melting range (90 - 120°C.) is consistent with the value to be expected for a highly branched sample.

4. A comparison of these structural parameters with those of linear polyethylene indicates that short chain branching is present.

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